

1-1-1, Sonoyama, Otsu-shi, Shiga

(72) Inventor: Jyun Kohama

c/o Shiga Division of Toray Industries, Inc.

1-1-1, Sonoyama, Otsu-shi, Shiga

(54) [Title of the Invention]

Method for Manufacturing Organic Electroluminescent Element

(57) [Abstract]

[Problem]

To provide a method for manufacturing an organic electroluminescent element of fine pattern precision without a wet process.

[Means for Solution]

A method for manufacturing an organic electroluminescent element having a light emitting layer made of an organic compound between an anode and a cathode, comprising the step of a patterned portion included in the element is formed through a mask which is sticking to a substrate by a magnetic force.

[Claims]

[Claim 1]

A method for manufacturing an organic electroluminescent element having a light emitting layer made of an organic compound between an anode and a cathode, comprising the step of:

forming a patterned portion included in the element through a mask which is sticking to a substrate by a magnetic force.

[Claim 2]

The method for manufacturing the organic electroluminescent element according to Claim 1, wherein the mask exerted by attractive force from a magnetic field is placed over an obverse side of the substrate; and a magnetic field source is placed over a reverse side of the substrate.

[Claim 3]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has at least one kind of elements of Fe, Co, and Ni with a composition ratio of 1 % or more in total.

[Claim 4]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has at least one kind of elements of Fe, Co, and Ni with a composition ratio of 20 % or more in total.

[Claim 5]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has a thickness of 2 mm or less.

[Claim 6]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has a thickness of 500 μm or less.

[Claim 7]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has a shortest pattern pitch of 2 mm or less.

[Claim 8]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the mask has a shortest pattern pitch of 500 μm or less.

[Claim 9]

The method for manufacturing the organic electroluminescent element according to Claim 2, wherein the magnetic field source is an electromagnet.

[Claim 10]

The method for manufacturing the organic electroluminescent element according to Claim 2, wherein the magnetic field source is a permanent magnet.

[Claim 11]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein at least one of the anode or the cathode is a transparent electrode.

[Claim 12]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein a transparent anode is formed over a transparent substrate.

[Claim 13]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the patterned portion is a light emitting layer.

[Claim 14]

The method for manufacturing the organic electroluminescent element according to Claim 13, wherein the light emitting layer is formed by an evaporation method.

[Claim 15]

The method for manufacturing the organic electroluminescent element according to Claim 1 or 2, wherein the patterned portion is at least one of the anode or the cathode.

[Claim 16]

The method for manufacturing the organic electroluminescent element according to Claim 15, wherein the anode or the cathode is formed by an evaporation method or a sputtering method.

[Claim 17]

The method for manufacturing the organic electroluminescent element according

to Claim 1 or 2, wherein a spacer is provided in a non-light emitting portion of the organic electroluminescent element.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an organic electroluminescent element which can change electrical energy into light. The organic electroluminescent element can be applied to a field such as a display element, a flat panel display, a back light, a light, an interior, a sign, an advertising display and an electrophotography machine.

[0002]

[Prior Art]

An organic electroluminescent element in which electrons injected from a cathode and holes injected from an anode recombine with each other to emit light in an organic fluorescent material between the electrodes has been actively researched in recent years. The element receives attention since it has features of being low-profile, and achieving bright light emission under a low driving voltage and multicolor light emission realized by selecting a fluorescent material.

[0003]

The bright light emission of the organic electroluminescent element was shown by C. W. Tang and others of Kodak Company for the first time (Appl. Phys. Lett. 51 (12) 21, p.913, 1987). A structure of the organic electroluminescent element shown by Kodak Company is typified by the structure in which a diamine compound having a hole transport property, 8-hydroxyquinolinealuminium as a light emitting layer, and Mg:Ag as a cathode are formed sequentially over an ITO glass substrate by an evaporation method. The organic electroluminescent element can emit green light of 1000 cd/m^2 at a driving voltage of approximately 10V. These days, although some organic electroluminescent elements vary their structures, for example, some organic electroluminescent elements include an electron transport layer in addition to the foregoing components, the structure of the organic electroluminescent element basically follows that of the Kodak Company's. Studies are conducted actively to apply the

organic electroluminescent element which can realize bright and multicolor light emission to a display element or the like.

[0004]

However, a serious problem of the organic electroluminescent element arises from patterning of the elements as indicated on Nikkei Electronics (No. 654 p.102, Jan. 29, 1996.)

[0005]

For example, in the case of a full color display, light emitting layers of R, G, and B are needed to be formed in predetermined positions. A patterning like this is usually carried out by a wet process such as a photolithography method, but the organic layer forming the organic electroluminescent element does not have high resistance to moisture, organic solvent, and chemical. It is possible to gain an element which can be formed by a wet process by selecting an appropriate organic material as disclosed in Japanese Patent Laid-Open No.H6-234969, but the organic material which can be employed is restricted.

[0006]

Further, it is essential to pattern an electrode in a display element. When an electrode over the organic layer is patterned by a wet process, the problem of damaging the organic layer arises as well.

[0007]

For those reasons, a dry process typified by an evaporation method is conventionally applied to manufacture the organic electroluminescent element. Patterning of the organic electroluminescent element is usually carried out by using a mask. That is, the mask is placed over the forward position of the substrate over which the element is manufactured, and the organic layer or the electrode is evaporated only in opening portions of the mask.

[0008]

[Problems to be solved by the Invention]

The mask needs to be thinner to correspond to a fine patterning. Since the mask is not strong enough, adhesion between the substrate and the mask deteriorates due to

bending or the like of the mask. In the conventional method, when the fine patterning carried out, the spreading of an evaporation material under the mask can not be ignored, and so patterning with high precision was difficult to be carried out. And those problems are serious since they can lead to short circuits of elements and crosstalk due to increased leak current. For example, according to Japanese Patent Laid-Open No.H2-66873, a pattern pitch of less than 300 μm is much smaller than a range of pixel size capable of being patterned with a mask.

[0009]

In view of the foregoing, it is an object of the present invention to provide a method for manufacturing the organic electroluminescent element with fine pattern precision which can not be formed by a wet process. That is, it is the object of the present invention to provide a method, not only to fix the mask to the substrate, but to achieve enough adhesion between the mask and the substrate to realize a fine patterning by the mask, which was impossible conventionally.

[0010]

[Means to solve the Problem]

To solve the foregoing problems, the present invention provides a method for manufacturing an organic electroluminescent element having a light emitting layer made of an organic compound between an anode and a cathode comprising the step of forming a patterned portion included in the element is formed through a mask which is sticking to a substrate by a magnetic force.

[0011]

[Embodiment]

An organic electroluminescent element according to the present invention is an element which has a light emitting layer made from an organic compound between an anode and a cathode, which emits light when electrical energy is applied. In this electroluminescent element, at least one of the layers such as the anode, the cathode, and the light emitting layer is patterned.

[0012]

The anode and the cathode need to have enough conductivity to supply a current

to the element to emit light. It is preferable that at least one of the electrodes is transparent to take light out.

[0013]

The transparent electrode does not arise any serious problem when it has a visible light transmittance of 30% or more. Ideally, the transparent electrode has a visible light transmittance of nearly 100%. Basically, it is preferable to have almost the same transmittance throughout the visible light region. When one wants to change color, it is possible to make the electrode absorb light deliberately. In that case, it is technically easier to change color by using a color filter or an interference filter. As a material for the transparent electrode, at least one element selected from indium, tin, gold, silver, zinc, aluminum, chromium, nickel, oxygen, nitrogen, hydrogen, argon, and carbon is used usually. Alternatively, it is possible to use an inorganic conductive material such as copper iodide or copper sulfide, or conductive polymer such as polythiophene, polypyrrole, or polyaniline. The material for the transparent electrode is not restricted to the foregoing materials.

[0014]

Examples of the anode which are particularly preferable for the present invention are tin oxide, zinc oxide, indium oxide, indium tin oxide (ITO), or the like, each of which is placed over the transparent substrate. As for the use in a display which is subject to patterning or the like, ITO which is excellent in workability is particularly preferable. ITO may contain a minor amount of metal such as silver or gold to reduce surface electrical resistance and control voltage drop. Alternatively, tin, gold, silver, zinc, indium, aluminum, chromium, or nickel can be used as a guide electrode for the ITO. Chromium is particularly preferable among them since it can serve as a black matrix and a guide electrode. It is preferable that ITO has low resistance in view of power consumption. An ITO substrate having resistance of 300 $\Omega/$ or less, for example, can serve as an element electrode. However, in consideration that a substrate of approximately 10 $\Omega/$ is supplied these days, a substrate of low resistance is particularly preferable to be used. Any thickness of ITO can be selected according to the value of resistance, even though ITO having a thickness of 100 to 300 nm is usually

used. A material for the transparent electrode is not particularly limited and a plastic plate or a film made of polyacrylate, polycarbonate, polyester, polyimide, or aramid may be used. A glass substrate can be nominated as a preferable example. Soda lime glass, alkali-free glass, or the like can be employed. It is enough that the transparent substrate has a thickness of 0.7 mm or more, which can keep mechanical intensity sufficiently. As properties of glass, alkali-free glass is preferable because it can minimize elution ion. Also soda lime glass with a barrier coat of SiO₂ or the like which is commercially available can be used. A deposition method of ITO is not exclusively restricted. An electron beam method, a sputtering method, a chemical reaction method, or the like can be employed.

[0015]

The cathode is not exclusively restricted as long as its material can inject electrons into the light emitting layer of the present element efficiently. Consequently, low work function metal such as alkali metal can be used. However, metal such as platinum, gold, silver, copper, iron, tin, aluminium, magnesium, or indium, or alloy of the foregoing metal and low work function metal can be nominated as preferable examples in consideration of the stability of the electrode. Alternatively, by depositing comparatively stable metal as the cathode over the organic layer pre-doped with a minor amount of low work function metal, a stable electrode which has high electron injection efficiency can be obtained. A method for manufacturing the electrode can be any dry process such as resistance heating evaporation, electron beam evaporation, sputtering, and ion plating. In the present invention, resistance heating evaporation is used since it can be performed easily.

[0016]

As the organic layer contained in the organic electroluminescent element, any of the following layers can be employed; 1) a hole transport layer/ a light emitting layer, 2) a hole transport layer/ a light emitting layer/ an electron transport layer, 3) a light emitting layer/ an electron transport layer, and 4) a light emitting layer in a form of a layer formed by mixing materials for the foregoing layers. That is, as long as an element structure includes a light emitting layer made of an organic compound, in

addition to the forgoing multilayers 1) to 3), a light emitting layer includes only a light emitting material or includes a light emitting material and a hole transport material or an electron transport material can be used.

[0017]

The transport layer is made of only a material having a hole transport property. Alternatively, the transport layer is made of a material having a hole transport property and polymer binder. As the material having a hole transport property, N,N'-diphenyl-N,N'-di(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD), or triphenylamines typified by N,N'-diphenyl-N,N'-dinaphthyl-1,1'-diphenyl-4,4'-diamine (NPD), tertiary amine such as N-isopropylcarbazol, or a pyrazoline derivative, a stilbene based compound, a hydrazone based compound, an oxadiazole derivative, a heterocyclic compound typified by a phthalocyanine derivative, or polymer such as polycarbonate with a side chain containing the foregoing monomers, a styrene derivative, polyvinylcarbazole, or polysilane are preferable but not exclusively.

[0018]

As a material for the light emitting layer, in addition to a known light emitting body like anthracene and pyrene, and the foregoing 8-hydroxyquinolinealuminium, for example, a bisstyrylanthracene derivative, a tetraphenylbutadiene derivative, a coumarin derivative, an oxadiazole derivative, a distyrylbenzene derivative, a pyrrolopyridine derivative, a perynone derivative, a cyclopentadiene derivative, an oxadiazole derivative, a tiadiazopyridine derivative, or polymer such as a polyphenylenevinylene derivative, a polyparaphenylene derivative, or a polythiophene derivative can be used. As a dopant doped into the light emitting layer, the foregoing rubrene, a quinacridone derivative, phenoxazone 660, DCM1, perynone, perylene, coumarin 540, a diazaindacene derivative, or the like can be used without being processed.

[0019]

A material having an electron transport property is required to transport efficiently electrons from the cathode in an area between electrodes applied with an electric field. Therefore, a material which can inject electrons effectively and which can transport the injected electrons effectively is preferable. Consequently, a material

with high electron affinity, high electron mobility, and high stability, which hardly generates impurities which become traps during manufacturing or in use is required. As a material satisfying the foregoing requirements, 8-hydroxyquinolinealuminium, hydroxybenzoquinolineberyllium, an ozadiozole derivative such as 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (t-BuPB), an ozadiozole dimer derivative with improved thin film stability such as 1,3-bis(4-t-butylphenyl-1,3,4-oxadiazolyl)biphenylene (OXD-1), or 1,3-bis(4-t-butylphenyl-1,3,4-oxadiazolyl)phenylene (OXD-7), a triazole derivative, a phenanthroline derivative, or the like can be nominated.

[0020]

The foregoing materials for the hole transport layer, the light emitting layer, and an electron transport layer can form each the layer singly. Alternatively, the foregoing materials can be used in the state of being dispersed in polymer binder such as a solvent soluble resin typified by polyvinyl chloride, polycarbonate, polystyrene, poly(N-vinylcarbazole), polymethylmethacrylate, polybutylmethacrylate, polyester, polysulfen, polyphenyleneoxide, polybutadiene, a hydrocarbon resin, a ketone resin, a phenoxy resin, polysulfone, polyamide, ethylcellulose, vinyl acetate, an ABS resin, and a polyurethane resin, or a hardening resin typified by a phenol resin, a xylene resin, a petroleum resin, a urea resin, a melamine resin, a unsaturated polyester resin, an alkyd resin, an epoxy resin, and a silicone resin, or the like.

[0021]

As the method for forming the foregoing organic layers such as the hole transport layer, the light emitting layer, and the electron transport layer, resistance heating evaporation, electron beam evaporation, a sputtering method or the like can be, but not exclusively employed. Resistance heating evaporation and electron beam evaporation are preferably used usually in consideration of their properties. Thicknesses of the layers depend on a resistance value of the organic layer and can not be specified. However, the thickness of the layer is selected empirically from 100 to 1000 nm.

[0022]

Electrical energy mainly refers to a direct current. However, a pulsed current

and an alternating current can be also used as electrical energy. A current value and a voltage value should be, but not exclusively, chosen so that the brightest luminance can be obtained with as low power consumption as possible in consideration of a lifetime of the element.

[0023]

A pattern portion according to the present invention basically refers to a portion involved in light emission of the organic electroluminescent element. If necessary, a non-light emitting portion which is formed to improve a contrast, pattern precision, or an electrical insulation property of the portion involved in light emission is patterned. Therefore, the light emitting layer, the anode, and the cathode are preferably subject to patterning.

[0024]

The light emitting layer and the electrodes are especially important among the portions involved in light emission. Shapes and sizes of those portions are not particularly restricted and the most suitable shapes and sizes are employed according to the application. For example, in the case that the light emitting layer and the electrode are used in a display element or a display, one pixel is formed by one or more light emitting regions specified by shapes of the patterned light emitting layer, electrodes, and non-light emitting region. That is, shapes and sizes of the patterned light emitting layer and electrodes in the present invention do not need to coincide with a shape and a size of a pixel. A shape of a pixel varies according to a display system such as a segment system or a dot-matrix system, but the size of a pixel is preferably 2 mm square or less. As for the use in a high definition display, a pixel has preferably a size of 500 μm square or less, more preferably, $100 \times 300 \mu\text{m}$ which is the same as that of a monochrome pixel used in a full color liquid crystal display which is commercially practical today can be nominated.

[0025]

As for the use in a display, patterned shapes of the light emitting layer and the electrode often have a repetition period. In that case, the shortest pitch of the patterned shape is preferably 2 mm or less, more preferably, 500 μm or less. The display may be

a passive matrix type or an active matrix type as typified by TFT type. The present invention does not restrict a particular structure and a driving method of a display.

[0026]

The foregoing electrode refers to at least one of the anode or the cathode of the organic electroluminescent element. Both of the electrodes may be patterned, if necessary, according to the present invention. Also, the foregoing electrode also refers to an electrode like a guide electrode which is added to improve conductivity of the electrodes. Basically, it is preferable that one electrode formed over the substrate is patterned by a wet process, then, after an organic layer is formed thereover, the other electrode is patterned by a method according to the present invention. It is more preferable example of a process in which a transparent electrode prepatterned over a transparent substrate is used as an anode, and an organic layer is formed thereover, then, a cathode formed over the organic layer is patterned according to the present invention.

[0027]

The non-light emitting portion which is patterned according to the present invention is not particularly restricted. The black matrix and an insulating layer for specifying the light emitting region can be nominated as preferable examples for the non-light emitting portion. The black matrix changes the color of a space between the light emitting regions into black to improve a contrast. The insulating layer protects an electrode edge, specifies the light emitting region, and improves conductivity between the electrodes. Materials, shapes, and sizes of both of the black matrix and the insulating layer can not be shown sweepingly, and the most suitable ones should be selected according to their uses.

[0028]

The mask of the present invention is a sheet type material such as a plate or a film which is provided with one or more opening portions. An organic material or an electrode material flies to a substrate by an evaporation method or the like, and the materials are deposited over the substrate through the opening portions of the mask which is placed over the forward position of the substrate. Thus organic electroluminescent element is patterned according to the shapes of the opening portions

of the mask.

[0029]

An important feature of the present invention is that adhesion between the mask and the substrate is improved by magnetic force. Therefore, the deformed portion of an evaporation material, that is, a portion in which the evaporation material is spread under the mask through the opening portions of the mask is decreased. And so a fine patterning which was unrealizable can be realized. It is not a primary object of the present invention neither to fix the position of the mask to the substrate nor to support the weight of the mask itself, so adhesion between the mask and the substrate can be improved by magnetic force, mechanical contact, or the like, and not exclusively restricted.

[0030]

In the present invention, as long as magnetic force is exerted between the mask and at least another material, the relationship between them is not exclusively restricted. For example, in the case that force of attraction by magnetic force is exerted between the mask and the substrate of the organic electroluminescent element, either or both of the substrate and the mask can be a magnet. Of course, an object on which the magnetic force exerts with the mask does not need to be the substrate. Similarly, either of attractive force and repulsive force can be employed instead of the magnetic force. A preferable example of the present invention is that a mask which is under the influence of force of attraction due to a magnetic field, that is, a mask which is made of a material attracted by a magnet is formed over the obverse side of the substrate over which the element is formed, and the mask is made stick to the substrate by a magnet formed over the reverse side of the substrate. The strength of the magnetic force varies according to the shapes, sizes, weights, or strengths of the mask, and so they can not be shown sweepingly. The strength of the magnetic field should be strong enough to obtain enough or more adhesion of the mask and the substrate when the mask is fixed by mechanical contact. When the mask is fixed by magnetic force, the strength of the magnet field should be strong enough to obtain enough or more adhesion of the mask and the substrate and to fix the mask to its position.

[0031]

As preferable examples of the magnet, a permanent magnet and an electromagnet can be nominated. Although the shape and the size of the magnet are not restricted exclusively, the size of the magnet is preferably larger than that of the opening portion of the mask so that force of attraction uniformly exerts to the whole opening portion of the mask in a vertical direction to the substrate. One magnet which generates a magnetic field which covers a required area may be used. Alternatively, a plurality of magnets bonded together, or a plurality of magnets aligned at regular intervals may be used. The distance between the magnet and the substrate is not exclusively restricted as long as the magnetic force can act sufficiently to the mask.

[0032]

As preferable examples of the material for a permanent magnet, a quench hardening magnet material such as pure iron, plain carbon steel, W steel, Cr steel, Co steel, or KS steel, a precipitation hardening magnet material such as MK steel, Alnico steel, NKS steel, or Cunico steel, a sintering magnet material such as OP ferrite, Ba ferrite, a material for a various kinds of rare earth magnet typified by SmCo series and NdFe B series can be, but not exclusively, nominated. The foregoing materials are often used bulk likely or they can be used as a magnet in a powdery state mixed into rubber or resin. Alternatively, the foregoing powdery material can be pressure formed.

[0033]

An electromagnet can be preferably used in the present invention since the electromagnet can control electrically ON or OFF of a magnetic field and magnetic force. Although a structure of the electromagnet is not exclusively restricted, a structure in which a solenoidal coil made by winding a conducting wire at several times and a magnetic core is put into the coil is particularly desirable. As a material for the magnetic core, in addition to the foregoing materials for a permanent magnet, a material for a metal magnetic core such as a silicon steel plate, Al-Fe alloy, or Ni-Fe alloy (permalloy), a material for ferrite magnetic core such as Mn-Zn series, Ni-Zn series, or Cu-Zn series, a material for a dust core, which is formed by compressing fine powder of a material such as iron carbonyl, Mo permalloy, or sendust with a bonding agent, can be

nominated. Such kinds of electromagnet may be used singly. Alternatively, a plurality of them may be used together as a magnetic field source.

[0034]

The foregoing magnetic materials can be also nominated as preferable examples of a material for the mask. The mask can be preferably formed by forming those materials into thin plate shapes. Alternatively, the mask can be also formed by forming powder of the magnetic materials mixed into rubber or resin into film shapes, and so the composition of the materials for the mask can not be specified sweepingly. In order to make magnetic force exerted sufficiently, the mask preferably contains at least one of the magnetic elements of Fe, Co, and Ni with a composition ratio of more than 1% in total (in the case of only one of the magnetic elements is contained, with the ratio of more than 1% by itself), more preferably, with a composition ratio of more than 20% in total. Attraction force exert to the manufactured mask. The mask may be magnetized or not from the beginning. The mask can be made from a magnetized material, or the mask can be magnetized after being manufactured as required.

[0035]

Shapes and sizes of the opening portions of the mask are basically the same as those of the patterned portions of the organic electroluminescent element. However, one patterned portion of the organic electroluminescent element can be corresponded by one mask at one time, by a plurality of masks at one time, or by one mask with shifts or the like at several times. Consequently, the patterns of the mask and those of the organic electroluminescent element do not need to coincide. As in the foregoing case that the organic electroluminescent element is used for a display, when a pattern having a repetition period is corresponded by one mask, the preferable pattern pitch of the mask is 2mm, more preferably, 500 μm .

[0036]

The thickness of the mask depends on the strength, size, and size of the pattern of the mask, and so can not be shown sweepingly. When the mask is thicker and stronger than it needs to be, big magnetic force is required to improve adhesion between the mask and the substrate, and it becomes difficult for the mask to follow a deformation of

the substrate. As a guide, a thickness of 2 mm of the mask or less is nominated as a preferable example. The present invention is particularly effective at a fine patterning process, and 500 μm is shown as a preferable example of the pitch of the pattern. In that case, when the opening portion has a width of 300 μm , the width of the space is 200 μm . To realize high quality pattern precision, the thickness of the mask is desirably less than five times as great as the width of the space (in this case, 200 μm), more preferably, the thickness of the mask is the same as the width of the space or less. Consequently, 500 μm or less is nominated as a particularly preferable example of the thickness of the mask corresponding to the fine patterning.

[0037]

In the case that the surface of the substrate used in the organic electroluminescent element is smooth, it is advantageous to use a mask with a smooth surface in order to obtain uniform adhesion between the mask and the substrate. However, when a thin mask is made to correspond to the fine patterning as described above, the mask easily deforms during its formation, and the mask tends to lose its smooth surface because of inequalities of the mask or the like. In that case, a process like annealing may be carried out to make the surface smoother. Further, the mask, which is often used in being fixed to a frame of a suitable shape, should be attempted to make its surface closer to the ideal state by fixing the mask under tension to the frame.

[0038]

In the manufacturing process according to the present invention, a spacer which serves as a cushion is preferably formed in the non-light emitting portion of the organic electroluminescent element. The spacer can prevent the mask from damaging the organic layer or the like which is formed over the substrate when the mask sticks with the side of the substrate over which the element is formed. The spacer can be used both as a spacer and a part or the whole of the black matrix. Although a manufacturing method or properties of a material for the spacer is not exclusively restricted, it is easier, in consideration of the process, to form the spacer over the substrate in advance by a photolithography method or the like in order to protect the light emitting portion from the mask sufficiently. The height of the spacer needs to be greater than the thickness

of the light emitting portion of the organic electroluminescent element and the spacer needs to have a height which does not cause deterioration of the pattern precision due to a spreading of the evaporation material. Usually, the spacer is formed to have the height of 0.5 to 100 μm , but not exclusively restricted and can be optimized according to the condition.

[0039]

The function of the foregoing spacer is also accomplished by forming a protrusion over a part of the portion of the surface of the mask in which the mask and the substrate contact to each other, and by making the protrusion get contact to the non-light emitting portion of the organic electroluminescent element, or by coating the whole mask with a relatively flexible material such as resin. Materials for the protrusion and the coating are not restricted exclusively, but it is easy that they are formed using photo resist or the like in consideration of a process.

[0040]

[Example]

Hereinafter, the present invention will be explained with examples and comparative examples, but the present invention is not limited to these examples.

[0041] Example 1

A mask of a kovar plate (a composition ratio: Fe=54%, Ni=29%, Co=17%) having a size of 28×36 mm and a thickness of 50 μm provided with opening portions formed by wet etching is prepared. Main part of one opening portion has a rectangular shape with the length of a shorter side of 200 μm and the length of a longer side of 15 mm. The 16 opening portions having the rectangular shapes are placed with a pitch of 300 μm in a shorter side direction. That is, the mask is a striped mask having 16 opening portions with pitches of 300 μm (the length of the opening portion 200 μm and the length of a space 100 μm) at their center parts. One of the opening portions is widened with a pitch of 1.27 mm (the width of the widened opening portion is 600 μm) within 7.5 mm in the longer side direction from both of the ends of the opening portion to make electrical connection to exterior portion easier. The mask is fixed to a stainless steel frame with a width of 2 mm in the same outside shape as that of the kovar

plate by laser welding. The mask is fixed in a vacuum deposition apparatus so that one surface of the kovar plate fixed to the stainless steel frame faces a deposition source (downward). A glass substrate having a size of 38×46 mm and a thickness of 1.1 mm and a magnetic shell having a size of 34×42 mm and a thickness of 3 mm are placed sequentially on the other surface of the kovar plate which faces upward. A rare-earth magnet (H-23CV) made by Hitachi metals, Ltd. is used as the magnetic shell. After the apparatus is evacuated into vacuum at 5×10^{-4} Pa or less, metal of Al is evaporated at a rapid rate of 1 nm/s to have a thickness of 150 nm by resistance heating vapor evaporation using an alumina crucible. During the evaporation, the substrate is rotated to make the film thickness smooth.

[0042]

FIG. 1 is a microscope photograph of Al electrodes evaporated over the surface of the glass substrate which is taken from the apparatus. The width of the electrode is 200 μm at the central point of the longer side. The value of resistance is measured by a tester using the portion where the pitch of the electrode is widened. There is no electrical short-circuits between the 16 electrodes, and a value of resistance between neighboring electrodes is 20 M Ω or more which is a measuring limit.

[0043] Comparative Example 1

When Al electrodes are patterned as in Example 1 except that the magnet is not used during the evaporation, an average of the width of the electrode is 270 μm (FIG. 2). However, a plurality of the Al electrodes become deformed and there are electrical short-circuits of ten pairs of neighboring electrodes among the 16 electrodes.

[0044] Example 2

Al electrodes are patterned as in Example 1 except that the width of the electrode is 250 μm and the width of the space is 50 μm (and so a pitch is 300 μm as in Example 1). FIG. 3 is a microscope photograph of evaporated Al electrodes. The width of the electrode is 255 μm . There is no electrical short-circuit between the electrodes, and the value of resistance between neighboring electrodes is 20 M Ω or more which is a measuring limit.

[0045] Comparative Example 2

When Al electrodes are patterned as in Example 2 except that the magnet is not used during the evaporation, every neighboring electrode overlaps each other, and so the width of each of the electrode is impossible to be measured (FIG. 4). And the value of resistance is measured to find that short-circuits are caused between every neighboring electrode.

[0046] Example 3

A glass substrate having a thickness of 1.1 mm and provided with an ITO transparent electrode film (made by electron beam evaporation, $15\Omega/\square$) is cut into some pieces to have sizes of 28×36 mm. ITO is patterned to be a $300\ \mu\text{m}$ pitch (the width of the ITO is $270\ \mu\text{m}$) \times 32 stripes by a photolithography method. One of the opening portions of the ITO stripe is widened with a pitch of 1.27 mm (the width of the widened opening portion is $800\ \mu\text{m}$) from either of the ends of the opening portion in the long side direction to make electrical connection to exterior portion easier. The substrate is washed and treated with UV-ozone. The substrate is fixed in a vacuum deposition apparatus, then the apparatus is evacuated into vacuum at 2×10^{-4} Pa or less. A hole transport material of bis(m-methylphenylcarbazol) is evaporated at a rapid rate of 0.3 nm/s to have a thickness of 120 nm, 8-hydroxyquinolinaluminium (Alq_3) doped with 0.35 wt% quinacridone is evaporated at a rapid rate of 0.3 nm/s to have a thickness of 30 nm, and Alq_3 is evaporated at a rapid rate of 0.3 nm/s to have a thickness of 70 nm, sequentially, from tantalum boat by a resistance heating method. The foregoing organic material is evaporated over the whole substrate. Then, a mask is fixed to the substrate so that ITO and the striped pattern of the electrodes form a right angle by using a magnet as in Example 1. Under vacuum the preformed organic layer is exposed to lithium vapor to be doped (1 nm in terms of film thickness), then Al is evaporated at a rapid rate of 0.5 nm/s to have a thickness of 150 nm.

[0047]

When the obtained passive matrix organic electroluminescence element of 32×16 pixel emits light line-sequentially, clear character display is realized. FIG. 5 is a microscope photograph of a light emitting region. One pixel has a size of 270×255

μm and each length of the side is corresponding to the width of actually patterned ITO and Al electrodes.

[0048] Example 4

A mask of a Ni plate having a size of 120×84 mm and a thickness of $25 \mu\text{m}$ provided with an opening portion is prepared as a mask for a light emitting layer. Fundamental form of the opening portion is a stripe shape that has a length of 67.2 mm and a width of $100 \mu\text{m}$. 272 pieces of the stripe shaped opening portions are aligned with a $300 \mu\text{m}$ pitch in the width direction. As FIG. 6 shows schematically, each stripe shaped opening portion 2a has crossover track 3 having a width of $20 \mu\text{m}$ at every 4.8 mm to prevent the deformation of the opening portion. A mask for a kovar plate having a size of 120×84 mm and a thickness of $100 \mu\text{m}$ provided with an opening portion formed by wet etching is prepared as a mask for a cathode. As shown in FIG. 7 schematically, each stripe shaped opening portion 2b has a length of 100 mm and a width of $270 \mu\text{m}$. 100 pieces of the opening portions are aligned with a $600 \mu\text{m}$ pitch in the width direction. The two kinds of masks are fixed to a stainless steel frame with a width of 2 mm which has the same outside shape as those of two masks by an electron beam welding method while paying attention to maintain their flatness.

[0049]

A glass plate 10 provided with an ITO transparent electrode film, which is the same glass plate as used in Example 3, is cut into some pieces to have sizes of 120×100 mm. The ITO is patterned to be a $100 \mu\text{m}$ pitch (the width of the ITO is $90 \mu\text{m}$) \times 816 striped shapes 20 by a normal photolithography method. Then, paste prepared by mixing a black pigment containing a condensation product of phthalosyanine oxide as its main component into nonphotosensitive polyimide is applied to the substrate by a spin coating method and the substrate is semi-cured under nitrogen atmosphere at a temperature of 140°C for 10 minutes in a clean oven. After the polyimide layer is patterned by a normal photolithography method using positive photo resist, the patterned polyimide layer is cured at a temperature of 280°C for 30 minutes to form a black layer having a thickness of $1.0 \mu\text{m}$ which serves as a spacer and a black matrix. As shown in FIG. 9, the black layer 30 has opening portions 31 having sizes of 70×250

μm and a center portion of the stripe shaped ITO 20 is exposed from the opening portions. The volume resistivity of the black layer is $10^8 \Omega\text{cm}$ or more so the black layer has a good insulating property.

[0050]

The substrate is washed and treated with UV-ozone. Then the substrate is fixed in a vacuum deposition apparatus and the apparatus is evacuated into vacuum at 2×10^{-4} Pa or less. Hole transport materials of Copper phthalocyanine is evaporated to have a thickness of 20 nm and bis(m-methylphenylcarbazol) is evaporated to have a thickness of 100 nm over the whole substrate to form a hole transport layer 32. Then, a mask for a light emitting layer is placed on the forward position of the substrate and a ferrite magnetic shell having a size of 110×100 mm, thickness of 10 mm, and residual magnetic flux density of 0.3T is placed on the backward position of the substrate. The mask and the ferrite magnetic shell are fixed on the substrate so that center lines of the stripe shaped opening portion 2a of the mask and the stripe shaped ITO stripe 20 of the substrate coincide with each other, and that the cross over track 3 does not interfere with the black layer opening portion 31. Under vacuum, as a blue light emitting layer 40, bis(2-methyl-8-hydroxyquinolinolato)-paraphenylphenolatoaluminium (BALq_3) doped with 0.3 wt% perylene is evaporated to have a thickness of 30 nm, and BALq_3 is evaporated to have a thickness of 70 nm, sequentially. The substrate and the magnetic shell are fixed to each other with 1/3 pitch shift of the mask. As a green light emitting layer 41, Alq_3 doped with 0.3 wt% quinacridone is evaporated to have a thickness of 30 nm and Alq_3 is evaporated to have a thickness of 90 nm sequentially over the stripe shaped ITO which is next to the one over which the blue light emitting layer 40 is evaporated. Similarly, as a red light emitting layer 42, Alq_3 doped with 0.3 wt % 4-(dicyanomethylene)-2-methyl-6-(paradimethylaminostyryl)-4-pyran (DCM) is evaporated to have a thickness of 30 nm and Alq_3 to have a thickness of 80 nm sequentially over the further next stripe shaped ITO. Light emitting layers of each color are placed on every third ITO 20 sequentially to cover the opening portion of ITO completely as shown in FIG. 10. Then, the mask for the light emitting layer is removed and Alq_3 is evaporated to have a thickness of 20 nm over the whole substrate

as a coating layer for the light emitting layer 43. Then, a mask for a cathode is placed on the forward position of the substrate and the foregoing magnetic shell is placed on the backward position of the substrate. They are aligned so that a stripe shaped opening portion 2b forms a right angle with the stripe shaped ITO 20 of the substrate and coincides with a center of the black layer opening portion 31. After the preformed organic layer is exposed to lithium vapor to be doped (1 nm in terms of film thickness) under vacuum, Al is evaporated to have a thickness of 200 nm to form a cathode. At this step, a cathode 50a has a pitch of 600 μm (the width of the cathode is 275 μm) as shown in FIG. 11. The substrate and the magnetic shell are fixed to each other with 1/2 pitch shift of the evaporation mask for a cathode. Similarly, Li is doped and an Al cathode is evaporated to form a cathode 50b having the same width as that of the cathode 50a in the gaps between the firstly evaporated cathodes. As shown in FIGs. 12 and 13 schematically, a passive matrix color display in which 816 pieces of the light emitting layers of R, G, and B (red, green, and blue) are aligned sequentially and 200 pieces of cathodes respectively having a pitch of 300 μm are aligned to form a right angle with ITO is obtained finally. Since three light emitting regions of R, G, and B form one pixel, the display has 272×200 pixels with a 300 μm pitch. Further, in FIG. 13, the black layer 30 is thinner than a light emitting portion to make the explanation easier, but the black layer 30 is thicker than the light emitting portion actually, and so it serves as a spacer sufficiently which protects the light emitting layer against contact with the mask.

[0051]

When the manufactured display emits light, each light emitting region R, G, and B emits light of its own color. Spreading of light due to intrusion of an evaporated material into another light emitting region during the evaporation is not observed. Short-circuits among stripe shaped cathodes are not observed, either. The size of the light emitting region is $70 \times 250 \mu\text{m}$ which is the same as that of the opening portion of the black layer. In addition, a clear pattern display and a multi-colored display are realized by line sequential driving.

[0052]

[Effect of the Invention]

According to the present invention, an organic electroluminescent element with fine pattern precision can be realized without wet processing.

[Brief Description of Drawings]

FIG. 1 is a microscope photograph of a pattern of a patterned Al electrode according to Example 1.

FIG. 2 is a microscope photograph of a pattern of a patterned Al electrode according to Comparative Example 1.

FIG. 3 is a microscope photograph of a pattern of a patterned Al electrode according to Example 2.

FIG. 4 is a microscope photograph of a pattern of a patterned Al electrode according to Comparative Example 2.

FIG. 5 is a microscope photograph of a pattern of a patterned pixel portion of an organic electroluminescent element according to Example 3.

FIG. 6 is a schematic plan view for explaining a mask for a light emitting layer used in Example 4.

FIG. 7 is a schematic plan view for explaining a mask for a cathode used in Example 4.

FIG. 8 is a schematic plan view for explaining an organic electroluminescent element of Example 4 (at the step of patterning ITO).

FIG. 9 is a schematic plan view for explaining the organic electroluminescent element of Example 4 (at the step of forming a black layer).

FIG. 10 is a schematic plan view for explaining an organic electroluminescent element of Example 4 (at the step of forming RGB light emitting layers).

FIG. 11 is a schematic plan view for explaining an organic electroluminescent element of Example 4 (at the first step of forming a cathode).

FIG. 12 is a schematic plan view for explaining an organic electroluminescent element of Example 4.

FIG. 13 is a cross-sectional view in AA' in FIG. 12.

[Description of the References Symbols]

1a and 1b mask portion
2a and 2b stripe shaped opening portion
3 cross over track
10 glass substrate
20 stripe shaped ITO
30 black layer
31 black layer opening portion
32 hole transport layer
40 blue light emitting layer
41 green light emitting layer
42 red light emitting layer
43 coating layer for light emitting layer
50a and 50b cathode

THIS PAGE BLANK (USPTO)